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The Phosphorus Selena Bromide α-$P_4Se_3Br_2$

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Dedicated to Professor Hans-Jörg Deiseroth on the Occasion of His 65th Birthday

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Abstract. Yellow crystals of the phosphorus selena bromide α-$P_4Se_3Br_2$ [monoclinic, $C2/c$, $Z = 8$, $a = 12.724(3)$ Å, $b = 14.732(3)$ Å, $c = 12.553(3)$ Å, $\beta = 116.60(3)°$] were obtained from the reaction of P_4Se_3 and bromine at 80 °C in sealed glass ampoules. The crystal structure features discrete molecules of the formula α-$P_4Se_3Br_2$ according to the well-known α-form of $P_4Ch_3I_2$ molecules (Ch = S, Se).

Introduction

Phosphorus chalcogena halogenides $P_xCh_yX_z$ (Ch = S, Se; X = Br, I) all consist of discrete small molecules, which can be formally derived either from an annular arrangement of phosphorus and chalcogen atoms or from the cage-like structure of P_4Ch_3 (Ch = S, Se) by substituting bridging atoms and adding terminal halogen atoms. Several of these compounds were characterized by single-crystal structure analysis such as α-$P_4S_3I_2$ [1–3], α'-$P_4S_3I_2$ [4] and β-$P_4S_3I_2$ [1, 5, 6], α'-$P_4Se_3I_2$ [4] and β-$P_4Se_3I_2$ [7], furthermore P_3Se_4I [8] and the exceptional $P_2S_6Br_2$ [9, 10]. However, the crystal structure of the latter shows some peculiarities. In addition, the preparation both of the α- and β-form of $P_4Ch_3X_2$ (Ch = S, Se; X = Cl, Br) was repeatedly reported [11–13]. These compounds were examined using solution NMR spectroscopy and X-ray powder diffraction, but still no single-crystal structure investigation of these compounds was reported.

The crystal structure of "α-$P_4Se_3Br_2$", containing the α-form of $P_4Ch_3X_2$ molecules, could now be determined. The packing of the molecules differs from the arrangement of molecules in the related compound α'-$P_4Se_3I_2$.

Results and Discussion

The title compound forms crystals containing molecules with the composition $P_4Se_3Br_2$. These molecules exhibit C_2 symmetry: Two dumbbells of phosphorus atoms and two selenium atoms are connected to a roof-shaped six-membered ring. The phosphorus atoms in the 1,4-positions are bridged by another selenium atom thus forming a norbornane analogue framework of P_4Se_3. The two remaining nonbridged phosphorus atoms are bound to bromine atoms. In another way the P_4Se_3 unit of the molecule can be understood as two five-membered rings sharing a common P–Se–P bridge. Two separate P–Se parts remain, and bromine is connected to each of the phosphorus atoms, see Figure 1. The molecular structure can also be formally derived from *catena*-P_4Se_4 [14], cutting the polymer into its repeating units and replacing the bridging selenium atoms by bromine.

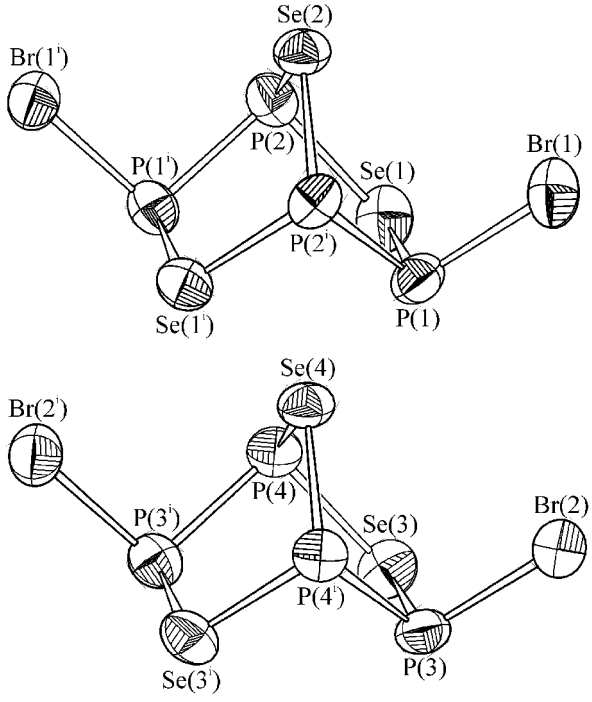

Figure 1. Molecules A (top) and B (bottom) in α-$P_4Se_3Br_2$. Ellipsoids enclose 50 % probability for atomic displacement. (*i*): $-x$, y, $0.5 - z$.

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The molecule exhibits the same structure as the well known α-$P_4Ch_3I_2$ molecules (*Ch* = S, Se) and therefore can be denoted as α-$P_4Se_3Br_2$. The IUPAC notation is 3,6-dibromo-2,5,7-triselena-1,3,4,6-tetraphosphabicyclo[2.2.1]heptane.

The common nomenclature of these molecules is less confusing relative to the phosphorus sulfides – the prefixes α and β only refer to the conformation of the molecule. An extra dash (cf. α'-$P_4S_3I_2$) indicates that there exist different polymorphs containing the same molecule. For $P_4Se_3I_2$, the only modification found containing α-type molecules is α'-$P_4Se_3I_2$, labeled in this way because it is isotypic to α'-$P_4S_3I_2$.

Two enantiomeric forms of the α-molecules exist, which both are present in the centrosymmetric crystal structure of α-$P_4Se_3Br_2$, i.e., the structure is consequently racemic.

In general, β-$P_4Ch_3X_2$ is energetically less favored and transforms irreversibly into α-$P_4Ch_3X_2$. Especially for bromides and chlorides this transformation already takes place in the solid state. A mechanism accounting for the formation and transformation of $P_4Ch_3X_2$ molecules from P_4Ch_3-halogen solution was proposed in [15].

Three types of bonds, P–P, P–Se, and P–Br, are present in α-$P_4Se_3Br_2$, with the average lengths of 2.21 Å, 2.27 Å, and 2.27 Å being typical for these types of bonds. However, the atomic distances within the two independent molecules in the crystal structure differ slightly, confer Table 4, which is likely caused by stacking effects.

The intramolecular distances between the transannular nonbonded P(1) and Se(1^i) or P(3) and Se(3^i) atoms, respectively, amount to 3.22 and 3.24 Å and are rather short relative to the sum of the van der Waals radii of the corresponding atoms (P: 1.90 Å; Se: 2.00 Å). This is also the case for α'-$P_4Se_3I_2$, where *Blachnik* et al. [4] attribute this observation to an extra stabilizing interaction.

The molecular arrangement in the crystal is shown in Figure 2. The α-$P_4Se_3Br_2$ molecules lie upon each other with an inverted orientation along [010], i.e. one selenium bridge tends up and the next one in this pile tends down. Orientation of the piles is reverted by the center of symmetry. Piles of molecules with alternating alignment of the bromine atoms result. These columnar piles are arranged in a pseudo-hexagonal rod pattern known as a typical packing scheme for linear polymer molecules. In α'-$P_4Se_3I_2$, the molecules are piled up in a similar way, but in contrast there is a tetragonal packing of piles in the crystal. The shortest intermolecular distances in α-$P_4Se_3Br_2$ are found between Br(1) and Se(3) with 3.62 Å, and between P(2) and Se(3) with 3.67 Å.

According to powder diffraction patterns [2, 4], a formal substitution of the chalcogen atoms in $P_4Ch_3X_2$ yields isotypic structures, e.g. the stacking of molecules is the same for β-$P_4S_3I_2$ [5] and β-$P_4Se_3I_2$ [7] and possibly also for α-$P_4S_3Cl_2$ and α-$P_4Se_3Cl_2$, or α-$P_4S_3Br_2$ and α-$P_4Se_3Br_2$, too. On substitution of the halogen in contrast there are structural changes due to the large difference in atomic size of the halogen and the consequential increase in density by rearrangement of the molecules [13, 15]. For "α-$P_4Se_3Br_2$" already unit cell parameters are given in reference [12] with a = 16.29 Å, b = 6.21 Å, c = 13.65 Å, and β = 105.17°, calculated from an X-ray powder diffraction pattern. These do not agree with the parameters found for α-$P_4Se_3Br_2$ reported herein. Possibly two or more polymorphs of α-$P_4Se_3Br_2$ exist, similar to α-$P_4S_3I_2$ and α'-$P_4S_3I_2$. However, we have no experimental evidence for the occurrence of a second modification of α-$P_4Se_3Br_2$.

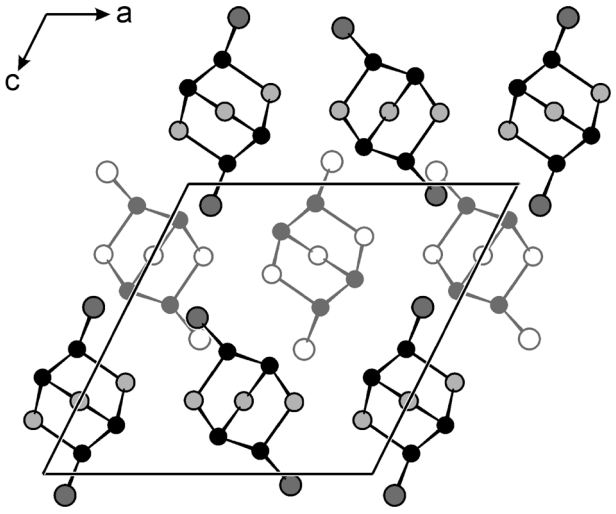

Figure 2. Projection of the crystal structure of α-$P_4Se_3Br_2$ along [010]; for the sake of clearness the unit cell is only half-filled with molecules. Phosphorus black, selenium light grey and bromine medium grey, with faded representation for molecules lying lower. Piles of molecules lying upon each other form a pseudo-hexagonal pattern.

The Raman spectrum of α-$P_4Se_3Br_2$ is displayed in Figure 3. It bears a marked resemblance to the Raman spectrum of α'-$P_4Se_3I_2$ [16], showing resonances in the range from 120 to 500 cm^{-1}. Because of the increased force constant, P–Br stretching modes are shifted to higher wave numbers relative to P–I stretching modes (especially bands at 328 cm^{-1} for α-$P_4Se_3Br_2$ and 308 cm^{-1} for α'-$P_4Se_3I_2$).

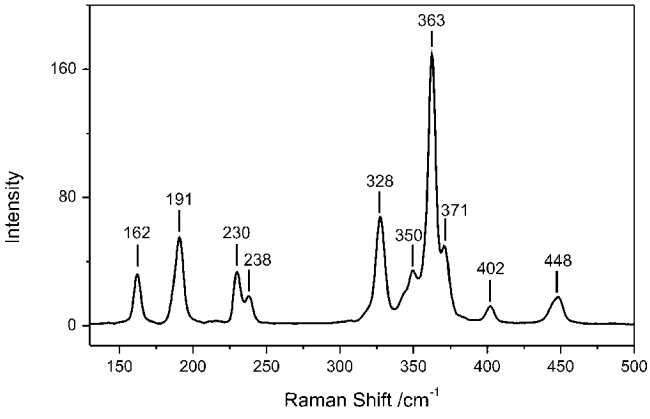

Figure 3. Raman spectrum of α-$P_4Se_3Br_2$ polycrystalline sample measured using a Nd:YAG laser with an excitation wavelength of λ = 1064 nm.

Experimental Section

Synthesis

In general, compounds $P_4Ch_3X_2$ can be obtained by halogenation of P_4Ch_3 (or even of the elements) with the corresponding halogen, di-

rectly or in solution. For a more convenient preparation of the chlorides and bromides, $P_4Ch_3I_2$ can be synthesized at first and then converted using metal halides, e.g. silver, bismuth or mercury halides [11, 12, 13].

Table 1. Crystallographic data and details of the structure refinement for α-$P_4Se_3Br_2$.

Formula	$P_4Se_3Br_2$
Molar mass /g·mol^{-1}	520.58
Crystal system, space group	monoclinic, *C* 2/*c* (No. 15)
Number of formula units *Z*	8
Temperature *T* /K	293(2)
Lattice parameters from single crystal data /Å resp. /°	
a	12.724(4)
b	14.732(4)
c	12.553(4)
β	116.60(3)
Cell volume *V* /Å^3	2104(1)
Calculated density ρ_{calc} /g·cm^{-3}	3.29
Crystal size /mm	0.29 × 0.17 × 0.14
Diffractometer	imaging plate diffractometer (IPDS-I, Stoe), graphite monochromator Mo-K_α radiation (λ = 0.71073 Å)
Range of data collection 2θ	4.5°–55.4° –16 ≤ *h* ≤ 16 –19 ≤ *k* ≤ 17 –16 ≤ *l* ≤ 16
Absorption correction	numerical with optical description of the crystal shape [18, 19]
Absorption coefficient μ (Mo-K_α) /mm^{-1}	18.62
No. of reflections collected (independent)	7694 (2443)
R_{int}, R_σ	0.053, 0.049
Structure solution	SHELXS 97 [20], direct methods
Structure refinement	SHELXL 97 [20], full-matrix least-squares method, refinement on F_o^2; anisotropic displacement parameters
No. of refined parameters	83
No. of restraints	0
Residual electron density /e·Å^{-3}	+ 1.24 / – 0.48
R_1 [$F_o > 4\ \sigma(F_o)$]	0.041
R_1 (all F_o)	0.069
wR_2 (all F_o)	0.090
GooF	0.92
Weighting parameters *a*, *b*	0.050, 0

Prior to the preparation of the title compound, vitreous phosphorus selenide P_4Se_3 was synthesized by heating red phosphorus (Hoechst, ultra pure grade) and grey selenium (chempur, 99.999+ %) in a molar ratio of 4:3 in an evacuated fused silica ampoule for three days to 300 °C and rapidly cooling down to ambient temperature. The brittle orange product was ground and used without further purification.

According to literature [17], bromine (Merck, extra pure, 0.2 mL, 7.8 mmol) and P_4Se_3 (1.2 g, 3.3 mmol) were filled into a fused silica ampoule under cooling with liquid nitrogen. After evacuation, the ampoule was sealed and afterwards slowly heated up to 80 °C. After four days it was cooled to ambient temperature within 10 hours. Yellow, rhomboidal crystals and microcrystals were obtained by this means. They appear to be light-sensitive, showing slow decomposition when being exposed to sunlight for several days. A closer investigation of this decomposition was not the topic of this work. The title compound is also sensitive to moisture, so all manipulations were performed in a dry argon atmosphere. However, X-ray powder diffraction shows the homogeneity of the reaction product. The compound can be manipulated at daylight but should be stored under argon and in the dark. Phase purity of the reaction product was checked by X-ray powder diffraction. The powder pattern exhibits solely the reflections for α-$P_4Se_3Br_2$.

Crystal Structure Determination

Reflection intensities of a single-crystal were collected with a Stoe imaging plate diffractometer IPDS-I. After applying a numerical absorption correction [18, 19], the crystal structure was solved by direct

Table 2. Atom coordinates and equivalent isotropic displacement parameters U_{eq}[a)] of α-$P_4Se_3Br_2$.

Atom	Wyckoff position	*x*	*y*	*z*	U_{eq} /Å^2
P(1)	8*f*	–0.0868(2)	0.2333(1)	0.0708(2)	0.0569(5)
P(2)	8*f*	0.1482(2)	0.1388(1)	0.3326(2)	0.0529(4)
P(3)	8*f*	0.3744(2)	0.0188(1)	0.0789(2)	0.0540(5)
P(4)	8*f*	0.4761(2)	0.1139(1)	0.3723(2)	0.0511(4)
Se(1)	8*f*	0.11135(7)	0.24183(6)	0.18504(8)	0.0666(2)
Se(2)	4*e*	0	0.03839(7)	0.25	0.0547(3)
Se(3)	8*f*	0.34648(7)	0.01148(6)	0.24659(7)	0.0619(2)
Se(4)	4*e*	0.5	0.21442(7)	0.25	0.0537(3)
Br(1)	8*f*	–0.10048(8)	0.13502(7)	–0.07438(7)	0.0715(3)
Br(2)	8*f*	0.23122(7)	0.11563(6)	–0.03851(8)	0.0686(2)

a) U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3. Tensor coefficients U_{ij}[a)] /Å^{2}of the anisotropic displacement parameters in α-$P_4Se_3Br_2$.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
P(1)	0.064(1)	0.054(1)	0.054(1)	0.0039(9)	0.0261(9)	0.0119(9)
P(2)	0.0444(8)	0.060(1)	0.051(1)	0.0023(8)	0.0183(8)	–0.0083(9)
P(3)	0.060(1)	0.047(1)	0.056(1)	–0.0022(8)	0.0272(9)	–0.0126(9)
P(4)	0.0570(9)	0.055(1)	0.050(1)	0.0007(8)	0.0315(8)	–0.0017(9)
Se(1)	0.0667(5)	0.0720(6)	0.0676(5)	–0.0241(4)	0.0359(4)	–0.0055(4)
Se(2)	0.0595(6)	0.0402(5)	0.0567(6)	0	0.0190(5)	0
Se(3)	0.0605(4)	0.0648(5)	0.0697(5)	–0.0149(4)	0.0373(4)	–0.0012(4)
Se(4)	0.0691(6)	0.0373(5)	0.0529(6)	0	0.0256(5)	0
Br(1)	0.0788(5)	0.0830(6)	0.0541(5)	–0.0190(5)	0.0310(4)	–0.0098(4)
Br(2)	0.0608(4)	0.0696(5)	0.0634(5)	0.0017(4)	0.0170(4)	–0.0042(4)

a) Coefficients U_{ij} of the anisotropic displacement factor tensor of the atoms are defined by $\exp[-2\pi^2(h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12} + ...)]$.

Table 4. Bond lengths in α-$P_4Se_3Br_2$.

Bond		Distance /Å	Bond		Distance /Å
P(1)	– P(2)	2.207(3)	P(3)	– P(4)	2.217(3)
	– Se(1)	2.279(2)		– Se(3)	2.289(2)
	– Br(1)	2.273(2)		– Br(2)	2.263(2)
P(2)	– Se(1)	2.275(2)	P(4)	– Se(3)	2.271(2)
	– Se(2)	2.251(2)		– Se(4)	2.250(2)

methods and refined against F^2 with anisotropic displacement parameters for all atoms using the SHELX-97 program package [20]. In Table 1 a summary of the crystal structure determination of α-$P_4Se_3Br_2$ is given. In Table 2 and Table 3 atom coordinates and displacement parameters are listed; atomic distances are given in Table 4.

Further data have been deposited with the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (E-Mail address: crysdata@fiz-karlsruhe.de), as supplementary material No. CSD-421007, and can be obtained by contacting the FIZ quoting the article details and the CSD number.

Raman Spectroscopy

Raman measurements on polycrystalline samples of α-$P_4Se_3Br_2$ were carried out with a Varian Fourier transform RAMAN Module coupled on a Varian FTS 7000e spectrometer equipped with a Nd:YAG laser (excitation wavelength λ = 1064 nm) and a liquid nitrogen cooled germanium detector. Samples were sealed in Duran glass capillaries of 1.5 mm outer diameter. The resolution was 1 cm^{-1}. The spectrum was processed with the Varian Resolutions Pro software [21].

Supporting Information (see footnote on the first page of this article): X-ray powder diffraction pattern of α-$P_4Se_3Br_2$.

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